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Appln. Serial No.: 10/632,245

Group Art Unit: 1754

Filing Date: August 1, 2003

Examiner: Langel, Wayne A.

Applicants: Cortright et al.

Attorney Docket No.: 09820.284

Title: **LOW-TEMPERATURE HYDROGEN PRODUCTION FROM OXYGENATED HYDROCARBONS**

**JOINT DECLARATION OF INVENTORS RANDY D. CORTRIGHT AND JAMES A. DUMESIC UNDER 35 USC §§1.131 and 1.132**

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

To the Commissioner:

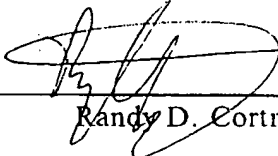
Your Declarants, Randy D. Cortright and James A. Dumesic, do hereby declare and state as follows:

1. We are each co-inventors of Claims 1-56 (as originally submitted and subsequently amended) of the above-identified patent application and are co-inventors of the subject matter described and claimed therein. As such, we are, individually and collectively, intimately familiar with the above-identified patent application and the subject matter claimed therein.
2. We have each read and are familiar with U.S. Patent No. 6,607,707, issued August 19, 2003, to Reichmann et al. The Reichmann et al. patent matured from an application for patent filed on August 15, 2001.

3. Our above-identified application for patent was filed on August 1, 2003, and claims priority as a continuation of U.S. application Serial No. 09/998,552, filed November 29, 2001 (and now issued as U.S. Patent No. 6,699,457). The earliest effective filing date of the present application is therefore November 29, 2001, a date which is less than one year from the August 15, 2001 filing date of the Reichmann et al. patent referenced in paragraph 2.
4. Prior to August 15, 2001, having earlier jointly conceived the idea of producing hydrogen at low temperatures via steam-reforming of oxygenated hydrocarbons, we prepared a confidential presentation for the Wisconsin Alumni Research Foundation (WARF), the assignee of the present application. (WARF is the patenting and technology transfer organization affiliated with the University of Wisconsin-Madison). A true and complete copy of that presentation is attached hereto as Exhibit A. Exhibit A is incorporated herein by reference. The entire presentation of Exhibit A was prepared and presented to WARF in a confidential meeting that took place at WARF's offices in Madison, Wisconsin, prior to August 15, 2001.
5. Exhibit A opens with a brief history of steam reforming of hydrocarbons to yield hydrogen and the uses for the resulting hydrogen. As noted at page A-1, for most industrial uses, including for ammonia synthesis, for oil refining, and for use as a fuel in fuel cells, hydrogen must have very low impurity levels of sulfur, CO, CO<sub>2</sub>, and water. Pages A-2 to A-6 of Exhibit A present an overview of the conventional steam reforming process, including a description of the water-gas shift (WGS) reaction. Page A-7 of Exhibit A outlines the disadvantages of conventional steam reforming of hydrocarbons (e.g., the hydrogen produced is contaminated with sulfur and CO; temperatures greater than 500 °C are required; the hydrocarbon reactants are highly flammable.)

6. Beginning at page A-8 of Exhibit A is a detailed description of the invention that is now recited in the claims pending in the present application. Specifically, at page A-8, the invention is briefly described as using oxygenated compounds such as ethanol, ethylene glycol, glycerol, and sorbitol (all of which are water-soluble oxygenated hydrocarbons having at least two carbon atoms as required by Claim 1) and reforming these compounds at low temperatures to yield hydrogen. Pages A-9 to A-12 describe using oxygenated hydrocarbon fuels have a C-to-O ratio of 1-to-1 and the favorable equilibrium constants that are obtained using these reactants. See the graphs at pages A-12 and A-13. Such compounds include ethylene glycol and sorbitol. The graph at page A-13 compares the equilibria between reforming of oxygenated compounds according to the present invention versus conventional reforming of hydrocarbons. The graph at page A-13 demonstrates that oxygenated compounds as recited in Claim 1 of the present application can be reformed to yield hydrogen at temperatures much lower than the temperatures required to reform hydrocarbons. Pages A-14 and A-15 describe the effect of temperature for steam reforming of oxygenates. As illustrated in the graph at page A-14, the reaction thermodynamics are favorable for the reforming of all oxygenates.
7. The remainder of Exhibit A, pages A-16 to A-21, is given over to a discussion of the effects of various catalysts, including catalysts containing the Group VIII transition metals ruthenium, rhodium, nickel, platinum, palladium, iridium, cobalt, and iron. See the graph at page A-17. This graph is significant in that it clearly shows the production of hydrogen by reforming ethylene glycol, in the presence of Group VIII transition metals, at a temperature of only 250 °C. The graph at page A-18 shows the corresponding results for a nickel catalyst supported on either a silica support (the red trace) or a mixed magnesia/alumina support (the blue trace). In both instances, hydrogen was produced. Pages A-19, A-20, and A-21 show corresponding traces for ruthenium/palladium catalysts, nickel/platinum catalysts, and nickel/palladium catalysts, respectively. In all instances, hydrogen was produced.

8. In closing, Exhibit A clearly demonstrates that we were in possession of the invention as broadly as it is now claimed prior to August 15, 2001.
9. All of the acts described herein and all of the work and experiments performed to generate the data in Exhibit A (and relied upon to antedate the Reichmann et al. patent) were performed in the United States, prior to August 15, 2001.
10. We, Randy D. Cortright and James A. Dumesic, individually and collectively, hereby declare that all statements made herein of our own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this Rule 131/132 Declaration is directed.

  
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Randy D. Cortright

September 22, 2004  
\_\_\_\_\_  
Date

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James A. Dumesic

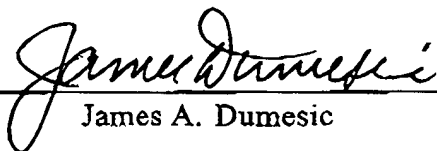
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Date

8. In closing, Exhibit A clearly demonstrates that we were in possession of the invention as broadly as it is now claimed prior to August 15, 2001.
9. All of the acts described herein and all of the work and experiments performed to generate the data in Exhibit A (and relied upon to antedate the Reichmann et al. patent) were performed in the United States, prior to August 15, 2001.
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Randy D. Cortright

Date



James A. Dumesic

Sept. 24, 2004

Date



# Low-Temperature Hydrogen Production from Steam-Reforming of Oxygenated Hydrocarbons

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Randy D. Cortright

and

James A. Dumesic

Department of Chemical Engineering  
University of Wisconsin- Madison

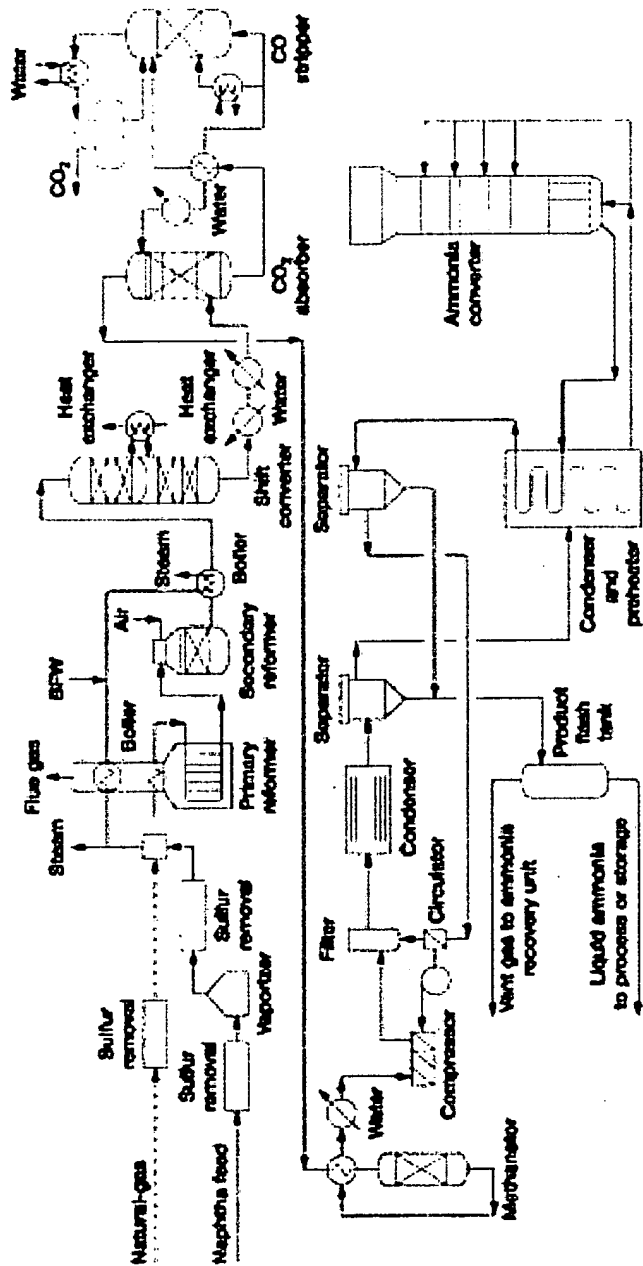
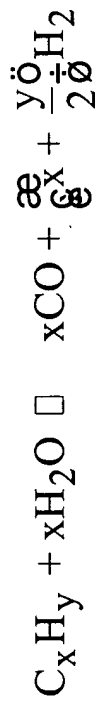


# Steam Reforming of Hydrocarbons

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- ↻ Hydrogen production for ammonia synthesis
  - ↻ Require low impurity levels of sulfur, CO, CO<sub>2</sub>, and H<sub>2</sub>O
- ↻ Hydrogen production for refining oil
  - ↻ Require low impurity levels of sulfur, CO, CO<sub>2</sub>, and H<sub>2</sub>O
- ↻ Hydrogen production for fuels cells
  - ↻ Require low impurity levels of sulfur and CO

# Steam Reforming Process (Utilizing Naphtha )



⇒ Reaction requires a metal to break C-C bond (Hydrogenolysis activity)



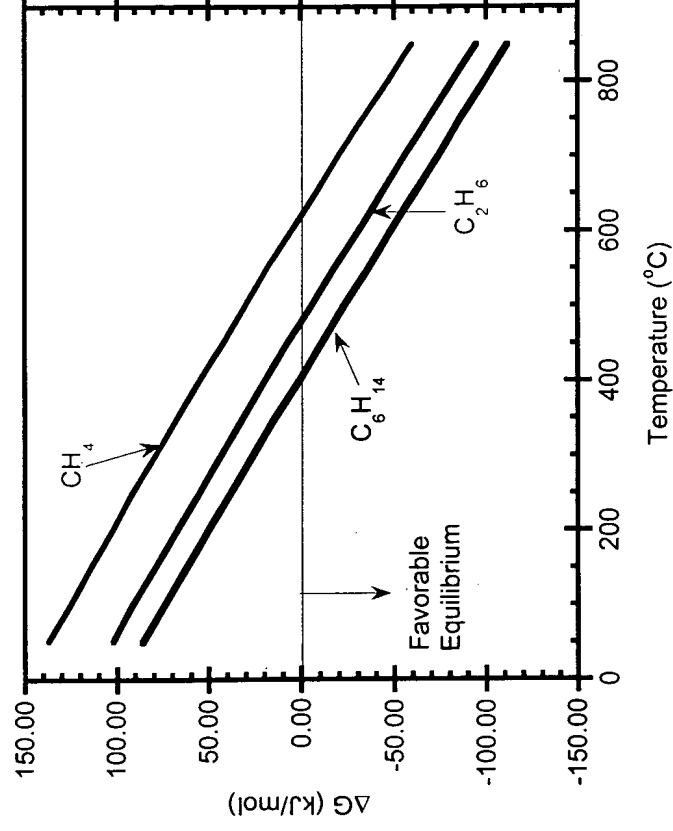
# Steam Reforming

(Conversion of Hydrocarbons to Hydrogen)

Steam reforming is the conversion of hydrocarbons (eg CH<sub>4</sub>) with steam to form CO and H<sub>2</sub>



- ⇒ Temperatures 500 – 850 °C
- ⇒ Catalyst - Ni on modified Al<sub>2</sub>O<sub>3</sub> (neutralized)
- ⇒ Catalyst sensitive to sulfur poisoning

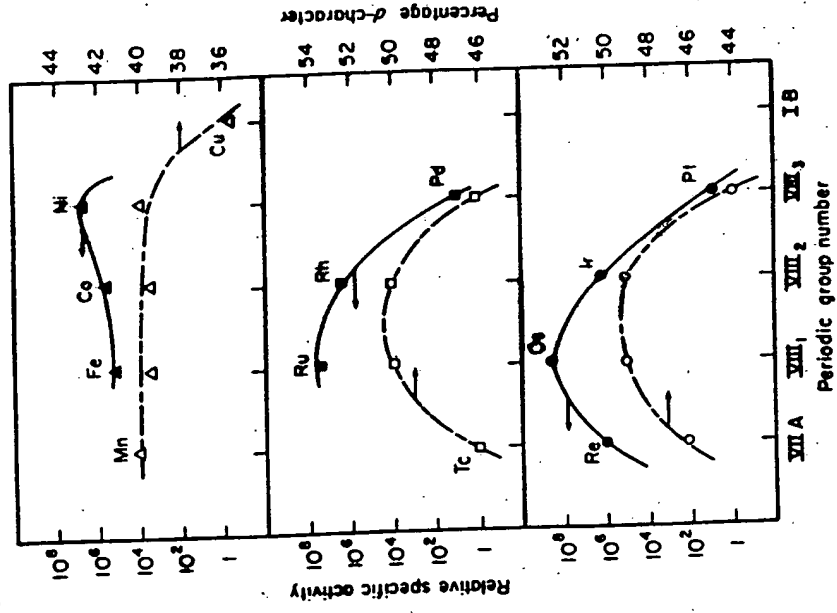


# Specificity in Catalytic Hydrogenolysis by Metals

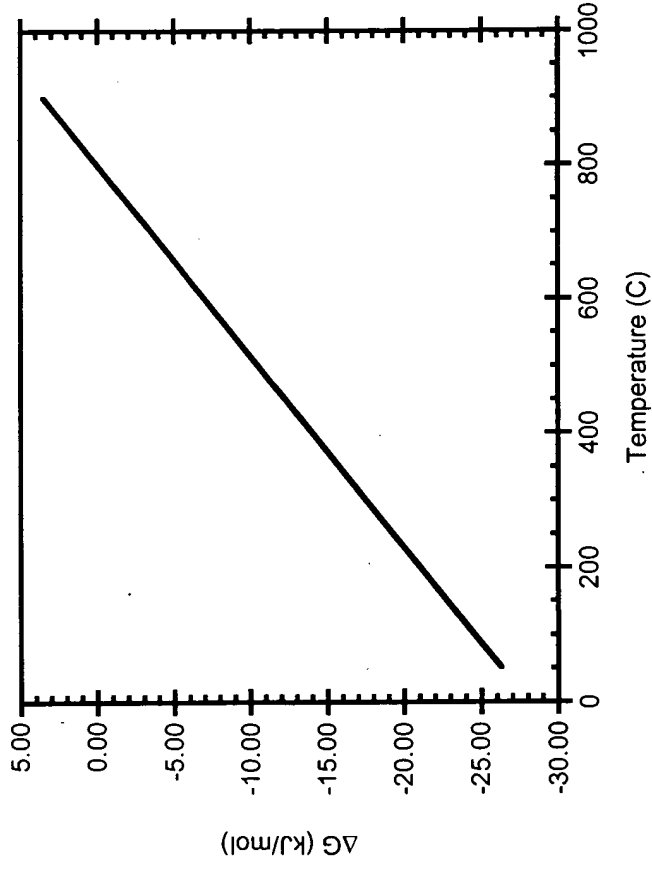
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## ☪ Volcano Plot – Ethane Hydrogenolysis

☪ [J.H. Sinfelt, Advances in Catalysis 23, 91 (1973)]



# Water-Gas Shift Reaction



- ⇒ Water gas-shift reaction uses steam to convert CO to  $\text{CO}_2$  and  $\text{H}_2$
- ⇒ High Temperature Water-Gas Shift over  $\text{Fe}_3\text{O}_4/\text{Cr}_2$  (350 – 450 °C)
- ⇒ Low Temperature Water-Gas Shift over Cu/ZnO (200 – 250 °C)

A-5

# Water-Gas Shift Catalyst

[Grenoble, Estadt, and Ollis, J. Catal. Volume 67, Page 90, 1981]

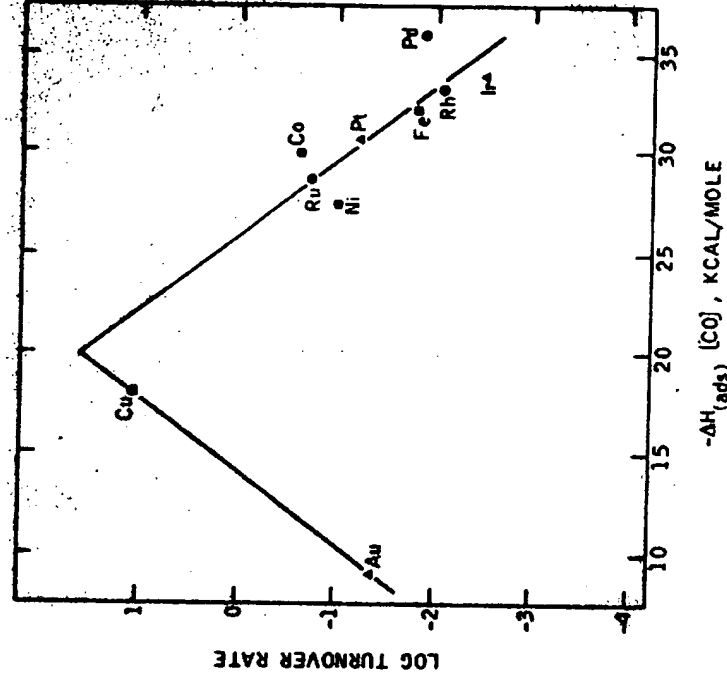


FIG. 2. Volcano-shaped relationship between metal turnover number at 300°C and heat of adsorption of carbon monoxide.

$\Rightarrow$  Cu/ZnO the preferred water-gas shift catalyst

# Disadvantages of Steam Reforming of Hydrocarbons

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- ↻ Hydrocarbons sources contain sulfur that must be removed via hydrotreating or adsorption.
- ↻ High temperatures (greater than 500 °C) required to overcome equilibrium constraints.
- ↻ Hydrocarbons are highly flammable
- ↻ For Fuel Cell Applications
  - ↻ Require a sulfur-free hydrogen source
  - ↻ For portable devices – desire non-flammable source
  - ↻ Require low carbon monoxide content

# Invention

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## ↻ Steam Reforming of Oxygenated Compounds

- ↻ Ethanol
- ↻ Ethylene Glycol
- ↻ Glycerol
- ↻ Sorbitol

## ↻ Oxygenated Compounds Sources

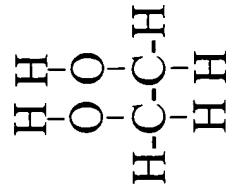
- ↻ Glycerol and Sorbitol are currently produced from renewable carbohydrates
- ↻ Ethylene glycol currently produced from ethylene, but can be produced from processing of carbohydrates

## ↻ Advantages

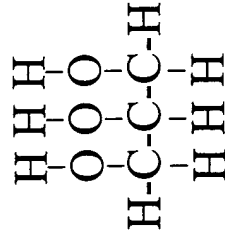
- ↻ Reforming of oxygenated compounds can occur at relatively low temperatures

# Oxygenates with C:O Ratio of 1:1

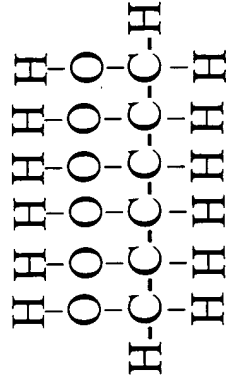
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Ethylene Glycol  
 $\text{C}_2\text{H}_6\text{O}_2$



Glycerol  
 $\text{C}_3\text{H}_8\text{O}_3$



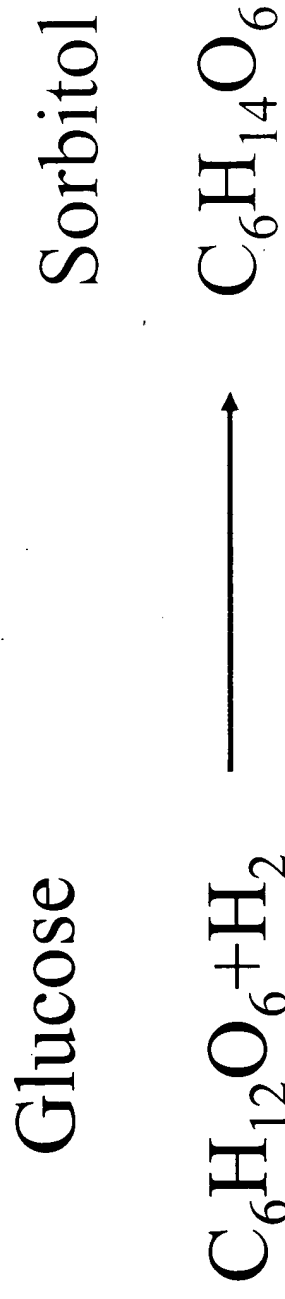
Sorbitol  
 $\text{C}_6\text{H}_{14}\text{O}_6$

$\Rightarrow$  C:O ratio of 1:1

$\Rightarrow$  Other compound with stoichiometry is methanol.

## Sorbitol from Glucose

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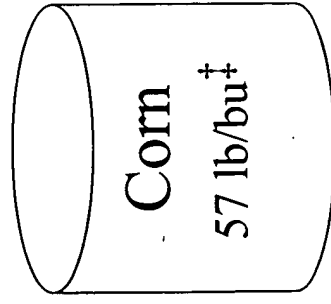


- $\Rightarrow$  Carbohydrates-Derived Compounds may be extracted from Renewable Biomaterials
- $\Rightarrow$  Mature Hydrogenation Technology
- $\Rightarrow$  Exhibit high yields of Sorbitol (greater than 99%).

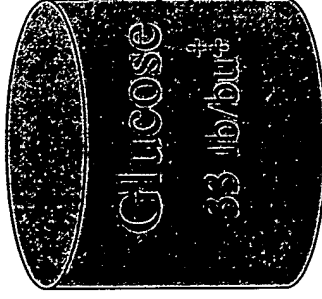


# Sorbitol Production from Corn Starch

\$2/bu

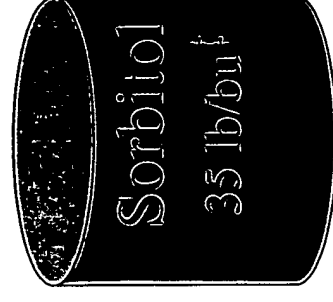


6.1 ¢/lb  
raw material cost



3 ¢/lb  
production cost

6.1 ¢/lb  
raw material cost



High Yield  
Hydrogenation

† Basis 1 bushel of corn

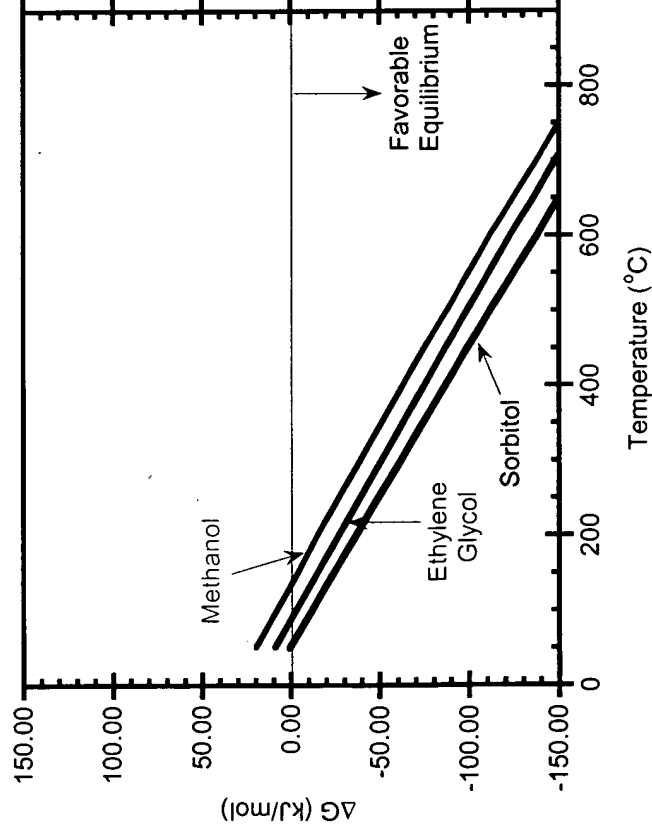
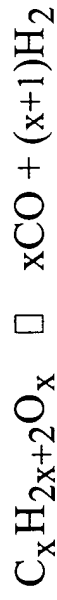
Current Lactic Acid

Prices 35 ¢/lb

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# Steam Reforming of Oxygenates with a C:O ratio of 1:1

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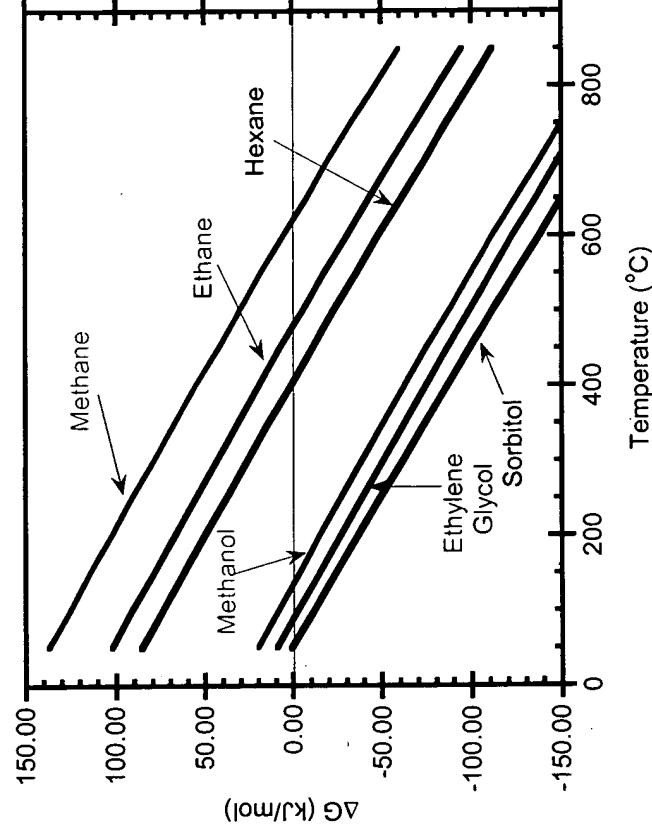
$\Rightarrow$  Equilibrium is favorable for methanol, ethylene glycol, glycerol, sorbitol at low temperatures.

A-12

# Reforming

## Oxygenates versus Hydrocarbons

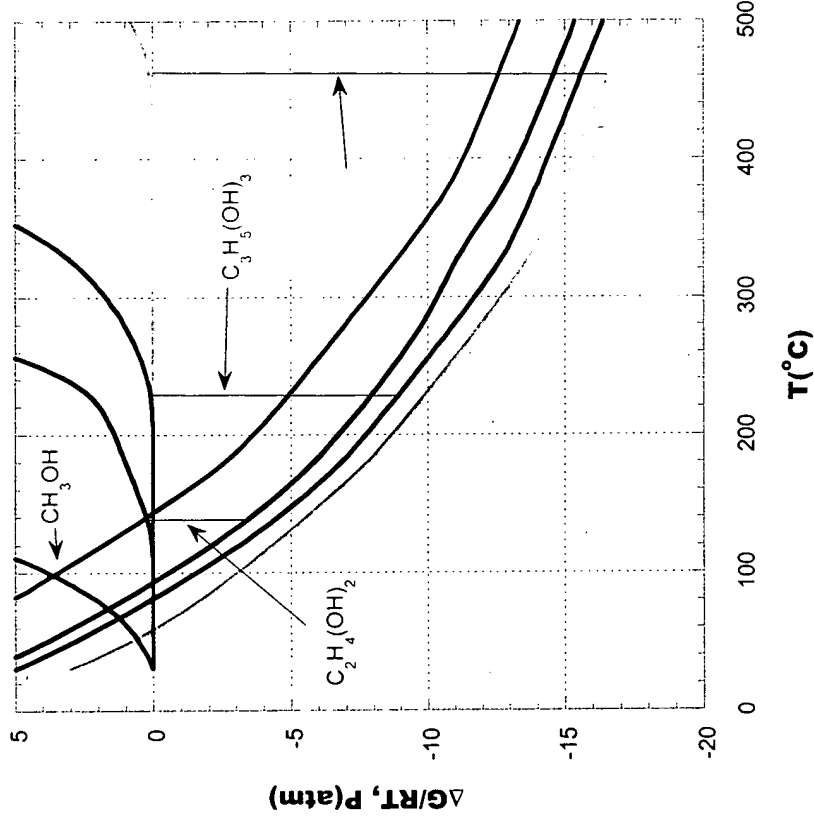
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$\Rightarrow$  Equilibrium is favorable for methanol, ethylene glycol, glycerol, sorbitol at low temperatures.

# Effects of Temperature for Steam Reforming of Oxygenates

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- ⇒ Reaction thermodynamics are favorable for reforming of all oxygenates
- ⇒ Phase thermodynamics dictate the reaction temperature because of the desire to do vapor-phase reforming.

# Steam Reforming of Ethylene Glycol

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0.2 cc/h of 10 wt % ethylene glycol with water

Catalyst	4% Pd/SiO2	4% Ru/SiO2	4% Pt/SiO2	4% Ir/SiO2
Amount (g)	0.1	0.1	0.1	0.1
Temperature	275	275	275	300

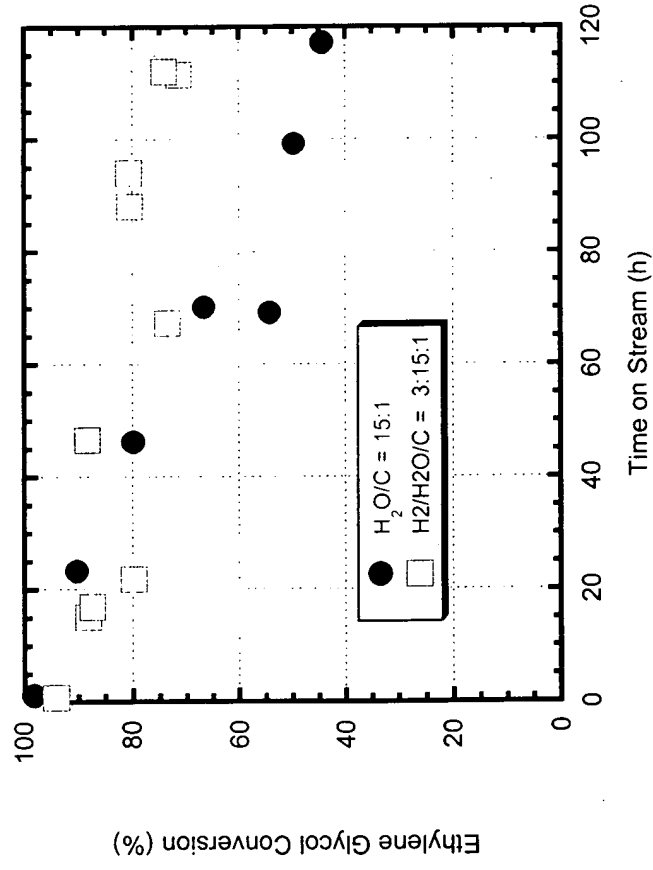
Conversions	100%	100%	100%	100%
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Product Ratio				
CO	100%	0%	37%	22%
Methane	0%	0%	0%	0%
CO2	0%	100%	63%	78%

# Stability for Steam Reforming of Ethylene Glycol over Ru

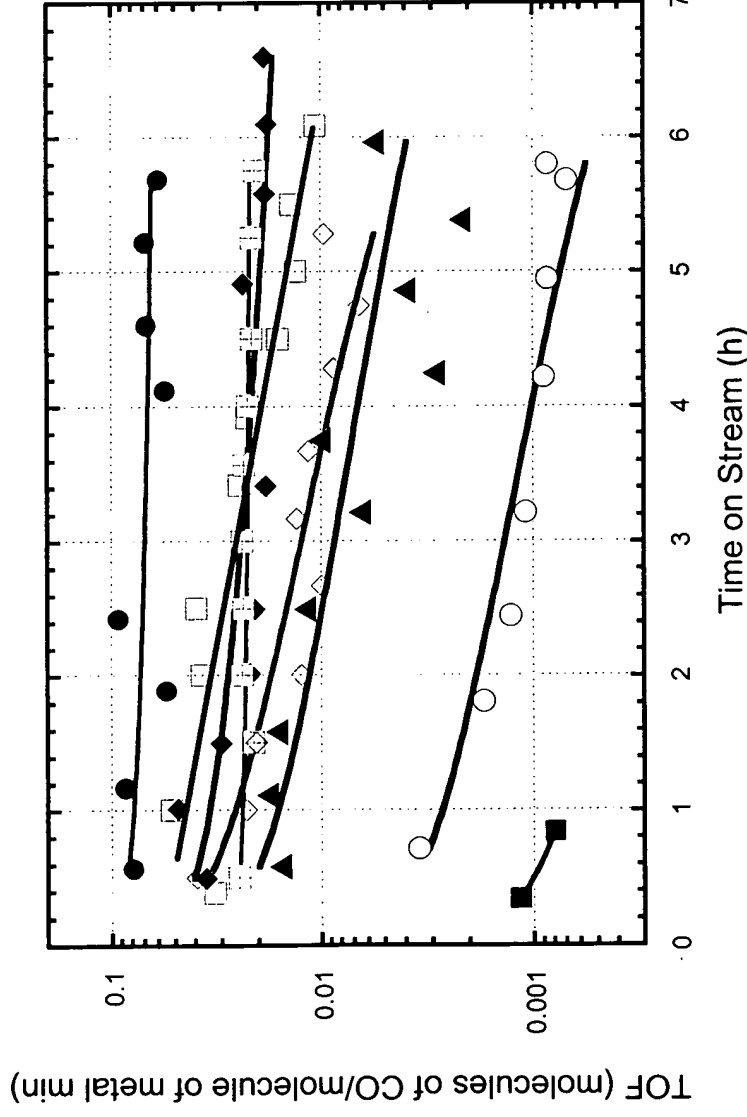
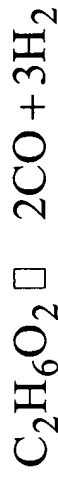
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Catalyst 4 wt% Ru/SiO<sub>2</sub>, 300 °C



- ⇒ Slow deactivation noted over Ru
- ⇒ Coking may be the deactivation mechanism

# Effect of Silica-Supported Metals on Reforming of Ethylene Glycol

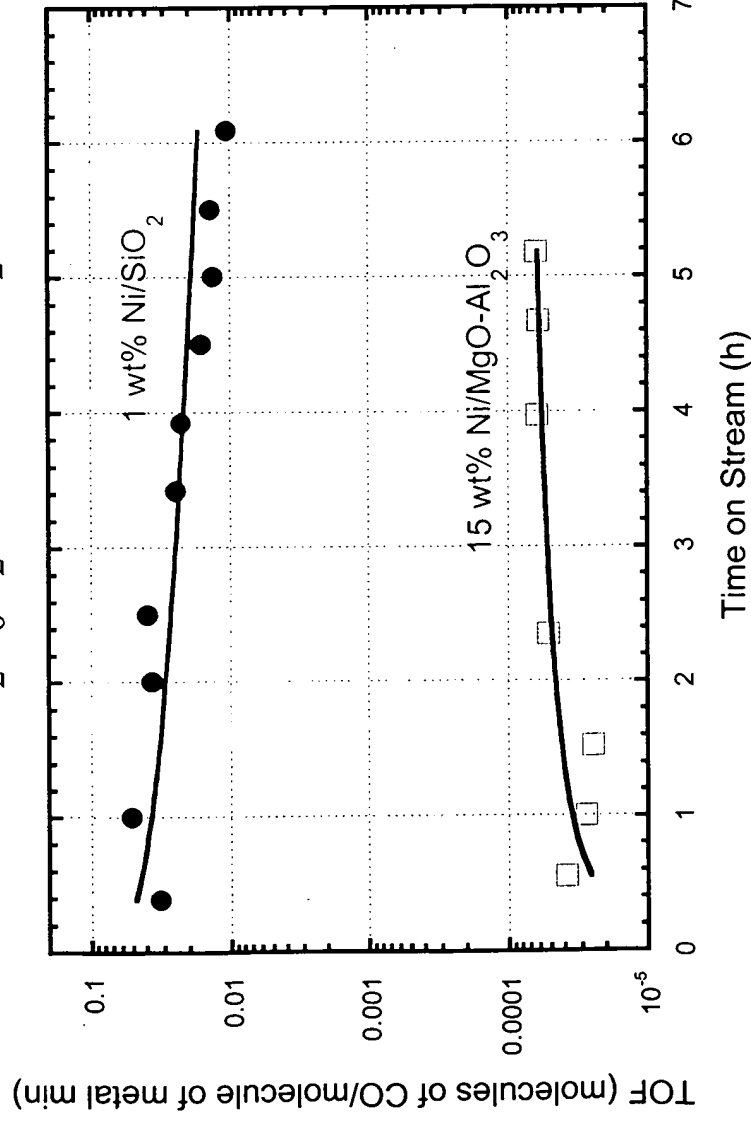
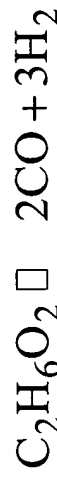


Silica-Supported Metals  
250 °C, 1 atm Pressure  
10 wt% EG in water  
0.2 cc/h of solution  
50 sccm of He

- ⇒ Rhodium most active and stable metal
- ⇒ Platinum and Palladium are both active and stable
- ⇒ Nickel initially more active, but exhibits less stable

# Effect of Support on Reactivity of Nickel for the Steam Reforming of Ethylene Glycol

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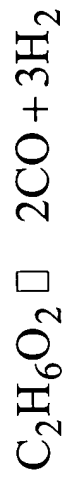


250 °C, 1 atm Pressure  
 10 wt% EG in water  
 0.2 cc/h of solution  
 50 sccm of He

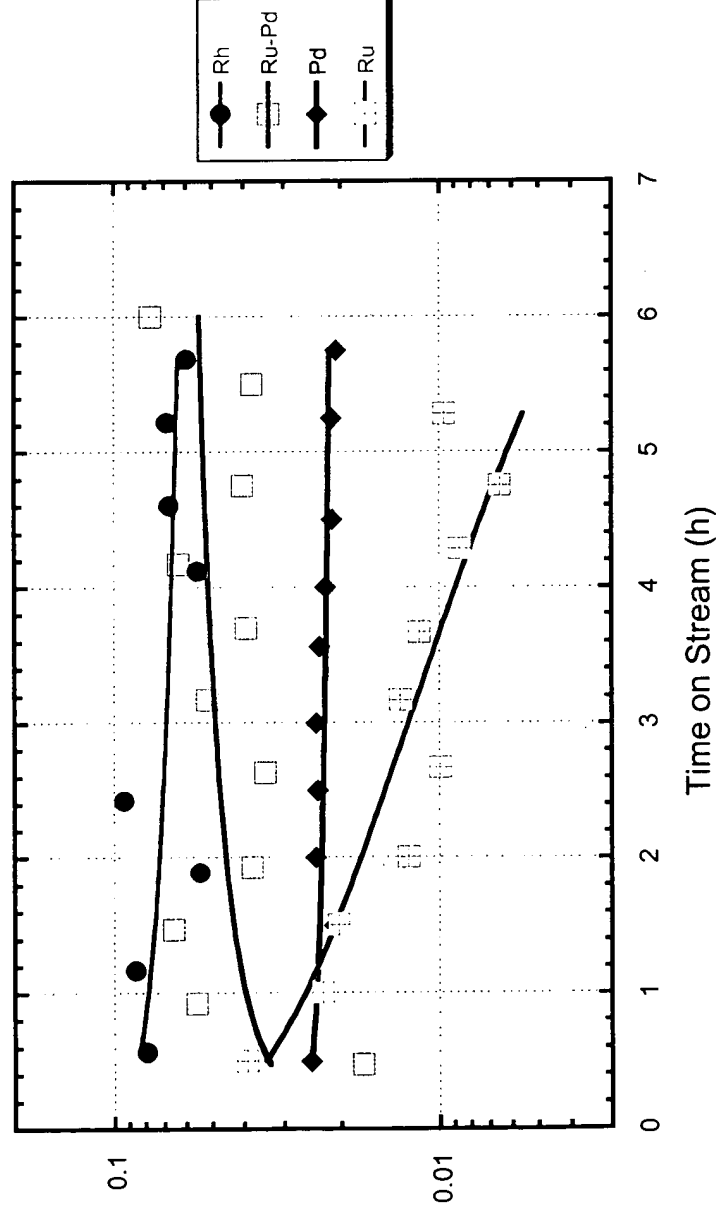
- ⇒ 15 wt% Ni/MgO-Al<sub>2</sub>O<sub>3</sub> – similar to hydrocarbon steam reforming catalyst.
- ⇒ Condensation products noted in reactor effluent indicating oxygenates were reacting with the support.



# Ruthenium-Palladium



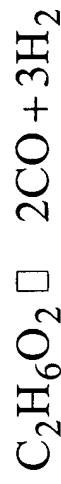
TOF (molecules of CO/molecule of metal min)



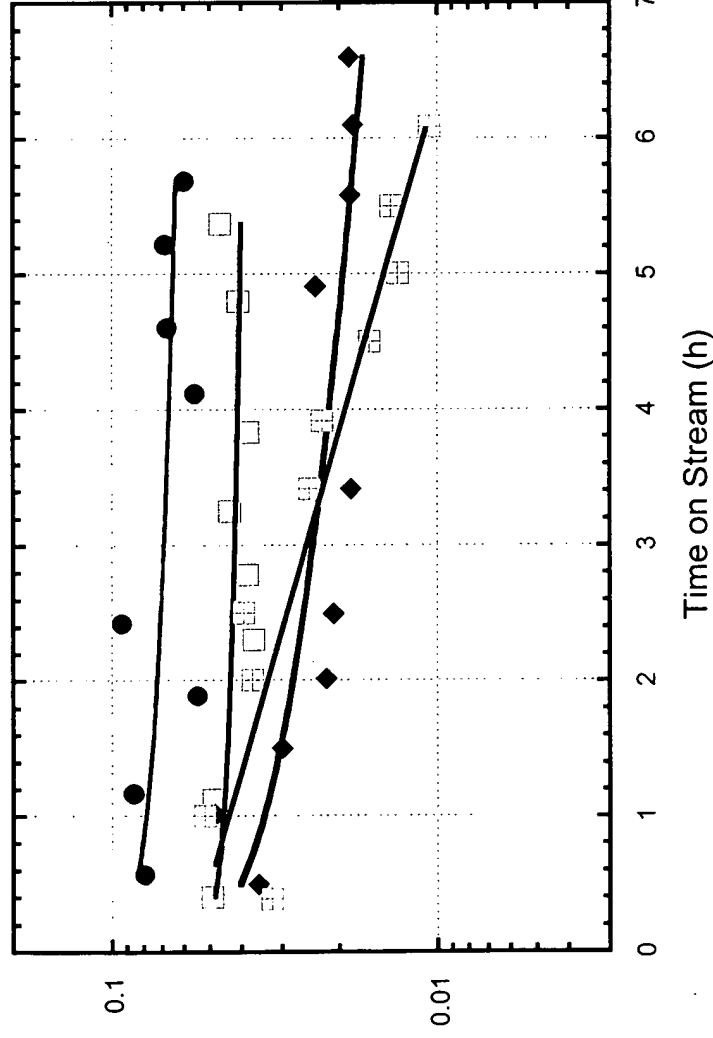
Silica-Supported Metals  
 250 °C, 1 atm Pressure  
 10 wt% EG in water  
 0.2 cc/h of solution  
 50 sccm of He

⇒ Ru-Pd bimetallic catalyst exhibits activity similar to rhodium

# Nickel-Platinum



TOF (molecules of CO/molecule of metal min)

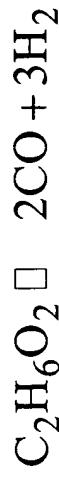


Silica-Supported Metals  
 250 °C, 1 atm Pressure  
 10 wt% EG in water  
 0.2 cc/h of solution  
 50 sccm of He

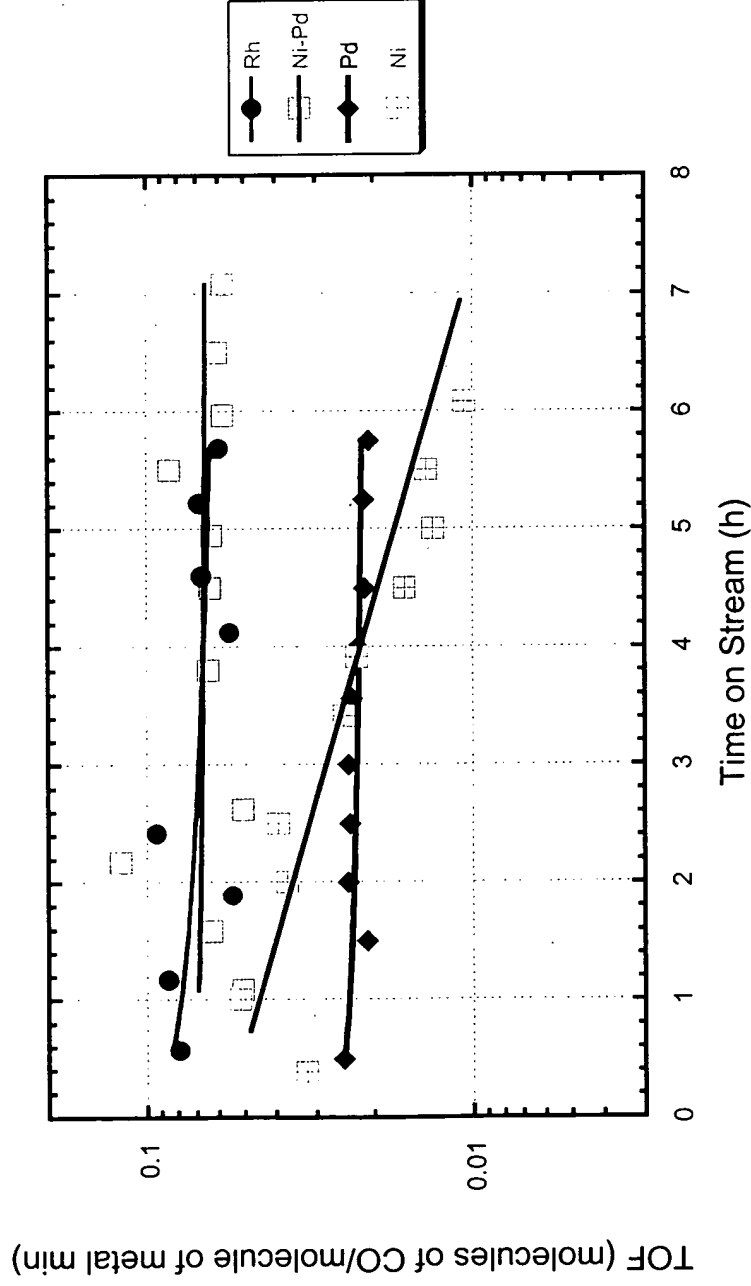
⇒ Ni-Pt bimetallic catalyst exhibits higher activity and stability than either Ni or Pt.

A-20

# Nickel-Palladium



Silica-Supported Metals  
 250 °C, 1 atm Pressure  
 10 wt% EG in water  
 0.2 cc/h of solution  
 50 sccm of He



- ⇒ Ni-Pd bimetallic catalyst exhibits activity similar to rhodium
- ⇒ Ni and Pd are both cheaper metals than Rh.

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